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Thermodynamic Properties of $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2

By J. M. Stuve, R. P. Beyer, and R. R. Brown



UNITED STATES DEPARTMENT OF THE INTERIOR



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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

cal	thermochemical calorie	kcal	kilocalorie
cal·mol ⁻¹	calorie per mole	kcal·mol ⁻¹	kilocalorie per mole
cal·mol ⁻¹ ·K ⁻¹	calorie per mole per kelvin	mol	mole (gram basis)
g	gram	pct	percent
h	hour	wt pct	weight percent
K	kelvin		

OTHER ABBREVIATIONS AND SYMBOLS USED IN THIS REPORT

°	standard reference state (superscript)	G _(T) [°]	Gibbs energy function at T
ΔH [°]	standard enthalpy change	R	Gas constant
ΔH _{f298} [°]	standard enthalpy of formation at 298.15 K	H _(T) [°]	Enthalpy function at T
C _p [°]	heat capacity with constant pressure	ln	logarithm using base e
T	temperature	(c)	crystalline or polycrystalline state
S ₂₉₈ [°]	Absolute entropy at 298.15 K		

THERMODYNAMIC PROPERTIES OF $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, AND CoS_2

By J. M. Stuve,¹ R. P. Beyer,² and R. R. Brown¹

ABSTRACT

In this Bureau of Mines investigation, the low-temperature heat capacities of polycrystalline phases corresponding to the sulfide compounds $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2 were measured by adiabatic calorimetry within the nominal temperature range 5 to 300 K. The derived absolute entropies S_{298}° were 10.36 ± 0.02 , 12.96 ± 0.03 , and 16.31 ± 0.03 $\text{cal} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, respectively, assuming third-law behavior. In addition, the standard enthalpy of formation ΔH_f° of $\text{CoS}_{0.89}$ was determined by bromine solution calorimetry. The derived value of ΔH_f° was -50.63 ± 2.1 $\text{kcal} \cdot \text{mol}^{-1}$, based on the ΔH_f° of CoO . This result is considerably more negative than previously published formation values based on high-temperature gas equilibrium studies.

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INTRODUCTION

This Bureau of Mines investigation is part of an integrated program to provide basic metallurgical data to further the efficient and economic utilization of mineral resources.

The cobalt-sulfur system provides a complex series of sulfides, some of which are metastable, nonstoichiometric phases at ambient temperatures. Chen and Chang (1)³ have recently studied the high-temperature phase relationships in the cobalt-sulfur system. There are three principal stable sulfide phases at ambient temperature, corresponding to the approximate ideal compositions of $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2 , respectively. Chen and Chang found that each of these compounds has a homogeneous range in the vicinity of ± 1 wt pct S, depending on the sulfur activity. The $\text{CoS}_{0.89}$ phase is stable to approximately $1,103 \pm 5$ K, $\text{CoS}_{1.33}$ to 943 K, and CoS_2 to $1,299 \pm 10$ K.

Most of the thermodynamic data available for the transition metal sulfides have been derived from solid-gas equilibrium studies at high temperatures. Among the more extensive of these are investigations by Rosenqvist (2), Alcock (3),

Kolbina (4), and Laffitte (5). No solution calorimetric investigations of the formation of $\text{CoS}_{0.89}$ could be found in the scientific literature.

Measurement of mid-temperature range heat capacities of $\text{CoS}_{1.33}$ has been previously reported by Schchelkotunov (6). Ogawa (7) and Waki (8) have reported segments of the low-temperature heat capacity data for CoS_2 . Tabular data were not given in these reports; therefore, evaluation of their results in relation to the present investigation can only be approximate, owing to the uncertainties in interpolation from their figures and graphs.

No low-temperature heat capacity data were found for $\text{CoS}_{0.89}$.

This investigation was originally planned to determine the formation enthalpies of $\text{CoS}_{1.33}$ and CoS_2 in addition to $\text{CoS}_{0.89}$. High-purity crystalline samples of these materials were prepared by pyrochemical methods; however, preliminary solution trials of the first two sulfides were unsuccessful owing to their very low rates of dissolution and reaction.

MATERIALS

Polycrystalline $\text{CoS}_{0.89}$ and CoS_2 were prepared by reaction of precisely measured stoichiometric amounts of sulfur with high-purity, 99.9+ pct cobalt powder or cobalt sulfides of intermediate composition in sealed silica tubes. Oxygen-free cobalt powder was obtained by treating a commercial metal powder of Co-CoO_x with hydrogen at 1,250 K. The sulfur was 99.999+ pct pure and was ground to a fine powder prior to mixing with the metal or sulfides. The tubes containing the reactant mixtures were purged with argon gas and evacuated prior to sealing.

The $\text{CoS}_{0.89}$ was prepared in two lots (100 and 144 g) by the following

procedure: The cobalt-sulfur mixture was initially heated to about 600 K to maintain a safe sulfur vapor pressure until most of the reaction was completed. The temperature was gradually increased to 775 K, for a total heating time of 120 h. Upon cooling, there was no evidence of free sulfur, indicating complete combination of the reactants. The silica tube was opened in an argon atmosphere dry box, and the sintered gray-black mass was ground to minus 100 mesh. The powder was transferred to a new silica tube, which was then sealed and heated for a final period of 120 h at 775 K. The final product was reground to a fine powder for calorimetric measurements. The X-ray diffraction pattern matched the pattern given on Powder Diffraction File (PDF) card 19-364 for cubic $\text{CoS}_{0.89}$.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

$\text{CoS}_{1.33}$ was prepared in a manner similar to that used for $\text{CoS}_{0.89}$. A stoichiometric quantity of cobalt and sulfur was initially reacted at 600 K. The temperature was increased to 785 K over a period of 2 days and held at this level for 42 h. The sample was ground and reheated for 115 h at 700 K. The product was determined to be single-phase polycrystalline cubic $\text{CoS}_{1.33}$. The X-ray diffraction pattern matched the pattern given on PDF card 19-367.

CoS_2 was prepared by reaction of a mixture of $\text{CoS}_{1.33}$ and $\text{CoS}_{1.87}$ with the stoichiometric amount of sulfur to adjust the composition to CoS_2 . The mixture was heated for 55 h at 573 K, 100 h at 758 K, 100 h at 710 K, 18 h at 873 K, and finally for 70 h at 673 K. The final heating was required to maximize the CoS_2 stoichiometry. The silica tube was removed and rapidly cooled on the tip end so that a trace of unreacted or equilibrium sulfur vapor would collect there. Chemical analysis indicated the composition to be $\text{CoS}_{1.973}$, and the X-ray diffraction pattern matched the pattern given on PDF card 19-362 for cubic $\text{CoS}_2(\text{c})$.

Emission spectrographic analysis of the sulfides indicated metallic impurities of nickel at <0.1 pct and aluminum, copper, iron, and silicon at <0.01-pct levels.

High-purity CoO was prepared from an initial mixture of Co_3O_4 and CoO made by oxidation of cobalt metal powder in a platinum boat at 1,275 K. This material was ground and given a final heating in oxygen at 1,375 K for 2 h, cooled to 1,275 K, purged with high-purity argon, and quenched rapidly to ambient room temperature to prevent formation of Co_3O_4 . X-ray analysis of the resulting powder indicated only the presence of $\text{CoO}(\text{c})$ phase. Spectrographic analysis did not detect any metallic elements other than

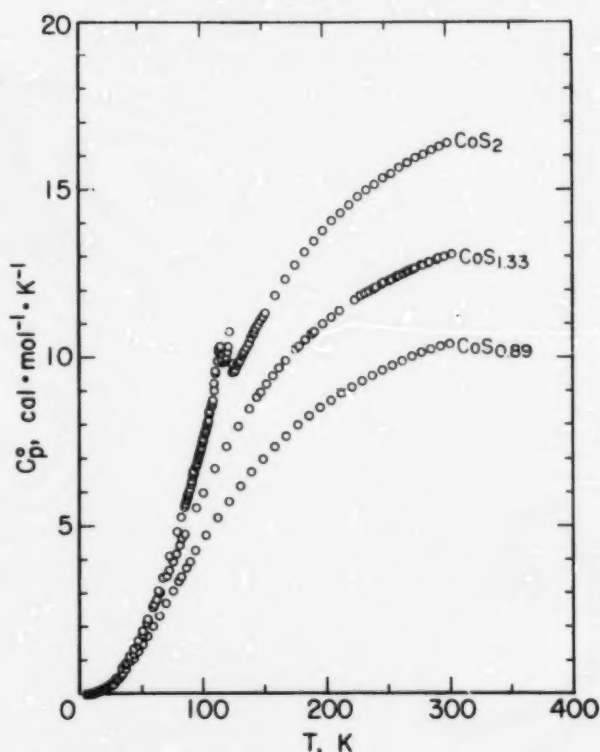


FIGURE 1. - Low-temperature heat capacities for $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2 .

aluminum, nickel, and silicon, all at the 0.005-pct level.

Cobalt metal for solution measurements was prepared at the Bureau in the form of high-purity electrolytic sheet. Strips were cut into convenient sizes without further treatment. No metallic impurities were detected by spectroscopy in this metal other than nickel, which was at the 0.05-pct level.

The solvent of 2.675 molal HBr and 1.319 molal Br_2 was prepared from distilled water and commercial analytical-grade reagents.

LOW-TEMPERATURE CALORIMETRY AND RESULTS

The automated adiabatic calorimeter used to measure the heat capacities has been described previously by Beyer (9). For $\text{CoS}_{0.89}(\text{c})$, a sample mass of 167.6867 g was used along with 1.5×10^{-4} mol He. For $\text{CoS}_{1.33}(\text{c})$, a sample of 194.4954 g

was used with 1.3×10^{-4} mol He. The sample of $\text{CoS}_2(\text{c})$ was 187.150 g with 1.3×10^{-4} mol He.

The experimental heat capacities for $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2 are shown in figure 1 and listed chronologically in

tables 1, 2, and 3. The temperature increment for each measurement can be calculated from temperatures tabulated for adjacent measurements. The overall uncertainty of the measurements was estimated to be ± 2 pct from 5 to 15 K, ± 1 pct from 15 to 50 K, ± 0.2 pct from 50 to 200 K, and ± 0.1 pct from 200 to 300 K.

TABLE 1. - Experimental low-temperature heat capacities of $\text{CoS}_{0.89}$

T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹	T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹
SERIES I		SERIES II	
5.01	0.003	80.65	3.339
5.53	.003	87.61	3.778
6.01	.004	95.30	4.247
6.62	.004	103.74	4.742
7.25	.009	112.65	5.236
7.92	.010	121.69	5.710
8.69	.013	130.83	6.164
9.59	.016	140.06	6.580
10.58	.021	149.36	6.968
11.66	.028	158.71	7.329
12.87	.037	168.12	7.655
14.18	.049	177.49	7.963
15.64	.061	186.68	8.240
17.20	.082	195.65	8.482
18.97	.115	204.43	8.701
20.88	.150	213.03	8.923
22.91	.195	221.50	9.106
23.54	.216	229.84	9.279
25.41	.269	238.06	9.435
27.37	.332	246.19	9.587
29.52	.406	254.23	9.733
31.83	.496	262.18	9.858
34.34	.603	270.07	9.986
37.06	.729	277.89	10.096
40.02	.873	285.66	10.201
43.39	1.050	293.37	10.289
47.06	1.254	301.04	10.359
50.91	1.476		
55.12	1.726		
59.72	2.018		
64.76	2.328		
70.26	2.696		
76.29	3.062		
82.91	3.480		
90.15	3.928		

TABLE 2. - Experimental low-temperature heat capacities of $\text{CoS}_{1.33}$

T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹	T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹
SERIES I		SERIES IV	
59.40	2.579	157.41	9.429
62.40	2.806	162.60	9.663
72.92	3.669	167.69	9.871
78.64	4.156	175.77	10.220
85.31	4.726	178.80	10.311
SERIES II		183.93	10.489
4.93	0.010	189.02	10.666
		SERIES V	
6.83	.015	183.84	10.495
9.96	.033	191.01	10.728
11.54	.047	198.04	10.949
12.45	.056	205.00	11.150
13.77	.070	211.78	11.341
15.19	.088	224.09	11.655
16.77	.111	228.55	11.780
18.49	.143	232.85	11.859
20.10	.175	239.40	12.006
21.61	.217	245.89	12.135
23.26	.264	252.34	12.242
25.04	.321	258.73	12.366
28.83	.470	SERIES VI	
36.59	.862	257.61	12.349
34.93	.801	263.97	12.440
37.36	.921	267.52	12.518
40.40	1.114	271.05	12.587
43.65	1.329	278.14	12.694
47.13	1.585	284.38	12.777
50.90	1.861	290.58	12.855
54.99	2.216	296.76	12.949
75.92	3.927	302.92	13.022
81.52	4.404	SERIES VII	
SERIES III		235.58	11.913
60.50	2.634	241.22	12.039
65.07	3.016	247.55	12.172
70.95	3.498	253.89	12.271
77.37	4.048	260.14	12.392
84.43	4.642	266.42	12.499
94.95	5.516	272.72	12.601
100.71	5.959	278.98	12.691
110.11	6.670	285.72	12.784
119.64	7.341	291.42	12.881
129.22	7.932		
138.29	8.462		
143.93	8.784		
147.50	8.948		
152.32	9.191		
157.35	9.427		
162.41	9.659		

TABLE 3. - Experimental low-temperature heat capacities of CoS_2

T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹	T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹	T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹	T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹
SERIES I		SERIES II		SERIES III		SERIES IV	
85.28	5.541	63.92	3.051	83.01	5.260	4.99	0.021
89.85	6.100	67.58	3.445	85.30	5.568	5.21	.025
97.69	7.120	73.25	4.094	86.22	5.646	5.70	.028
105.97	8.309	79.34	4.827	87.16	5.778	6.34	.032
133.09	10.071	86.11	5.633	88.09	5.908	7.08	.036
142.35	10.714	87.71	5.836	89.02	5.991	7.85	.043
151.18	11.304	89.56	6.062	89.96	6.104	8.71	.050
159.66	11.826	91.40	6.311	90.89	6.219	9.68	.057
167.86	12.302	93.24	6.538	91.82	6.322	10.75	.065
175.81	12.717	95.09	6.776	92.76	6.467	11.93	.075
183.56	13.092	96.94	7.012	93.69	6.613	13.23	.088
191.15	13.422	98.79	7.251	94.63	6.721	14.65	.102
198.59	13.730	100.64	7.498	95.56	6.828	16.21	.121
205.89	14.022	102.50	7.768	96.50	6.957	17.93	.144
213.08	14.258	104.35	8.031	97.44	7.117	19.80	.171
220.17	14.501	106.20	8.337	98.38	7.201	21.81	.207
227.17	14.737	108.06	8.644	99.32	7.311	23.81	.246
234.10	14.931	109.91	9.014	100.25	7.453	25.69	.301
240.95	15.107	111.74	9.530	101.19	7.569	27.36	.351
247.73	15.305	113.56	10.176	102.12	7.726	29.48	.421
254.46	15.439	115.42	10.110	103.06	7.840	33.28	.565
261.14	15.609	117.35	9.901	104.00	7.968	35.06	.652
267.77	15.752	119.26	9.987	104.93	8.126	37.80	.797
274.35	15.903	121.13	10.323	105.87	8.295	40.69	.974
280.89	16.002	124.87	9.783	106.80	8.393	43.83	1.193
287.40	16.135	126.65	9.599	107.74	8.554	47.21	1.449
293.88	16.241	128.55	9.749	108.67	8.721	50.88	1.754
300.33	16.348	130.44	9.866	110.79	9.220	54.86	2.114
		132.32	10.010	111.98	9.586	59.19	2.561
		134.21	10.155	112.90	9.878	63.90	3.033
		136.09	10.266	113.82	10.242		
		137.98	10.388	114.75	10.305		
		139.86	10.546	115.71	9.955		
		141.75	10.664	116.67	9.840		
		143.63	10.827	117.61	9.859		
		145.52	10.928	118.55	9.872		
		147.41	11.047	119.49	9.986		
		149.30	11.161	120.43	10.149		
		151.19	11.281	121.37	10.316		
				122.29	10.746		
				123.27	9.531		
				124.26	9.535		
				125.21	9.522		
				126.15	9.564		
				127.09	9.603		
				128.03	9.705		
				128.98	9.727		
				129.92	9.816		
				130.86	9.842		

The heat capacities for all three sulfides were smoothed using a curve-fitting computer program developed by Justice (10) to give the values of C_p° , $[S^\circ(T) - S^\circ(0)]$, $-[G^\circ(T) - H^\circ(0)]/T$, and $H^\circ(T) - H^\circ(0)$. These values are listed in tables 4, 5, and 6 for $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2 , respectively. The heat capacities for all three sulfides were graphically extrapolated from the lowest temperatures

of measurement to 0 K using a C_p°/T against T^2 plot.

A nonisothermal transition was observed for CoS_2 over the range 110 to 130 K. For this region, the calorimeter was operated in such a manner as to span the entire transition region in one measurement. The enthalpy of transition was calculated as $279 \text{ cal}\cdot\text{mol}^{-1}$.

TABLE 4. - Thermodynamic functions of $\text{CoS}_{0.89}$

T, K	C_p° , $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$S^\circ(T) - S^\circ(0)$, $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$-[G^\circ(T) - H^\circ(0)]/T$, $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$H^\circ(T) - H^\circ(0)$, $\text{kcal}\cdot\text{mol}^{-1}$
5	0.003	0.001	0.000	0.000
10	.019	.007	.002	.000
15	.055	.020	.005	.000
20	.133	.046	.012	.001
25	.257	.088	.023	.002
30	.424	.149	.038	.003
35	.632	.229	.060	.006
40	.873	.329	.087	.010
45	1.138	.447	.120	.015
50	1.421	.582	.160	.021
60	2.036	.894	.255	.038
70	2.684	1.257	.372	.062
80	3.316	1.657	.507	.092
90	3.929	2.083	.658	.128
100	4.517	2.528	.823	.170
110	5.076	2.984	.999	.218
120	5.603	3.449	1.183	.272
130	6.097	3.197	1.376	.330
140	6.557	4.386	1.574	.394
150	6.982	4.853	1.777	.461
160	7.372	5.316	1.984	.533
170	7.730	5.774	2.193	.609
180	8.055	6.225	2.405	.688
190	8.351	6.669	2.618	.770
200	8.619	7.104	2.831	.855
210	8.862	7.531	3.045	.942
220	9.083	7.948	3.258	1.032
230	9.285	8.356	3.471	1.124
240	9.471	8.756	3.683	1.217
250	9.644	9.146	3.894	1.313
260	9.805	9.527	4.103	1.410
270	9.959	9.900	4.311	1.509
273.15	10.006	10.016	4.376	1.541
280	10.107	10.265	4.517	1.609
290	10.250	10.622	4.721	1.711
298.15	10.364	10.908	4.887	1.795
300	10.387	10.972	4.924	1.814

TABLE 5. - Thermodynamic functions of $\text{CoS}_{1.33}$

T, K	C_p° , $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$S^\circ(T)-S^\circ(0)$, $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$-[G^\circ(T)-H^\circ(0)]/T$, $\text{cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$	$H^\circ(T)-H^\circ(0)$, $\text{kcal}\cdot\text{mol}^{-1}$
5	0.010	0.009	0.004	0.000
10	.034	.022	.010	.000
15	.085	.044	.017	.000
20	.174	.080	.028	.001
25	.320	.133	.043	.002
30	.527	.209	.064	.004
35	.786	.309	.092	.008
40	1.091	.433	.126	.012
45	1.434	.581	.168	.019
50	1.805	.751	.218	.027
60	2.607	1.150	.339	.049
70	3.438	1.614	.488	.079
80	4.280	2.129	.660	.118
90	5.109	2.681	.853	.164
100	5.903	3.261	1.065	.220
110	6.650	3.859	1.292	.282
120	7.344	4.467	1.531	.352
130	7.981	5.081	1.780	.429
140	8.559	5.694	2.038	.512
150	9.082	6.302	2.302	.600
160	9.553	6.904	2.571	.693
170	9.976	7.496	2.843	.791
180	10.357	8.077	3.118	.893
190	10.700	8.646	3.394	.998
200	11.011	9.203	3.671	1.107
210	11.294	9.747	3.947	1.218
220	11.553	10.279	4.223	1.332
230	11.790	10.798	4.497	1.449
240	12.008	11.304	4.771	1.568
250	12.209	11.799	5.042	1.689
260	12.393	12.281	5.311	1.812
270	12.561	12.752	5.578	1.937
273.15	12.611	12.898	5.662	1.977
280	12.714	13.212	5.842	2.063
290	12.853	13.660	6.104	2.191
298.15	12.958	14.018	6.316	2.296
300	12.982	14.098	6.363	2.320

SOLUTION CALORIMETRY AND RESULTS

Enthalpy of solution measurements were obtained using an adiabatic solution calorimeter previously described by Stuve (11-12). The calorimetric sequence of solution reactions used to derive ΔH_f° of $\text{CoS}_{0.89}(\text{c})$ is given in table 7. The actual enthalpy measurements were based on dissolution of 0.002 mol of $\text{CoS}_{0.89}(\text{c})$ and respective stoichiometric quantities

of $\text{S}(\text{c})$ (orthorhombic), $\text{CoO}(\text{c})$, and $\text{H}_2\text{O}(\text{l})$. The acidic bromine solvent used for each solution measurement consisted of 738.3 g of 2.675-molal HBr and 155.6 g liquid bromine. Solution measurements were done at 315 ± 0.5 K. Corrections to 298 K were applied by estimation of ΔC_p of reactions 1, 2, and 3.

TABLE 6. - Thermodynamic functions of CoS_2

T, K	C_p° , cal·mol ⁻¹ ·K ⁻¹	$S^\circ(T)-S^\circ(0)$, cal·mol ⁻¹ ·K ⁻¹	$-[G^\circ(T)-H^\circ(0)]/T$, cal·mol ⁻¹ ·K ⁻¹	$H^\circ(T)-H^\circ(0)$, kcal·mol ⁻¹
5	0.024	0.022	0.011	0.000
10	.059	.049	.023	.000
15	.107	.082	.037	.001
20	.176	.121	.053	.001
25	.279	.171	.071	.002
30	.435	.234	.093	.004
35	.651	.317	.119	.007
40	.931	.421	.150	.011
45	1.276	.550	.187	.016
50	1.679	.705	.231	.024
60	2.629	1.093	.341	.045
70	3.728	1.579	.482	.077
80	4.901	2.153	.654	.120
90	6.124	2.800	.856	.175
100	7.420	3.512	1.085	.243
¹ 110	9.027	4.288	1.341	.324
¹ 130	9.831	6.709	2.070	.603
140	10.546	7.464	2.428	.705
150	11.222	8.215	2.789	.814
160	11.846	8.959	3.152	.929
170	12.412	9.695	3.515	1.051
180	12.921	10.419	3.878	1.177
190	13.378	11.130	4.241	1.309
200	13.789	11.827	4.603	1.445
210	14.161	12.509	4.964	1.585
220	14.499	13.176	5.322	1.728
230	14.808	13.827	5.677	1.874
240	15.090	14.463	6.030	2.024
250	15.349	15.085	6.380	2.176
260	15.585	15.691	6.727	2.331
270	15.800	16.284	7.070	2.488
273.15	15.863	16.467	7.177	2.538
280	15.996	16.862	7.409	2.647
290	16.176	17.426	7.745	2.808
298.15	16.313	17.876	8.016	2.940
300	16.343	17.977	8.077	2.970

¹Nonisothermal transition.

Experimental results for the enthalpies of solution of $\text{CoS}_{0.89}(\text{c})$, $\text{CoO}(\text{c})$, and $\text{S}(\text{c})$ are summarized in reactions 1, 2, and 3 of table 7, respectively. The heat of dilution of $\text{H}_2\text{O}(\text{l})$ in the solvent, represented by reaction 6, was estimated from data by Wagman (13). Enthalpy of formation data for reactions 5, 7, and 9 were also taken from Wagman. The $\text{CoO}(\text{c})$ formation data of reaction 8 was selected

by Cyr (14) based on a recent critical evaluation of available values.

The ΔH_f° of $\text{CoS}_{0.89}(\text{c})$, represented by reaction 10, is equal to the sum of enthalpies of reactions 1 through 9, as written. The uncertainties of reactions 1, 2, and 3 were calculated as twice the standard deviation of the mean, according to Rossini's recommendations (15). The overall uncertainty in reaction 10 is the

square root of the sum of the squares of the uncertainties of reactions 1 through 9.

The calorimetric reaction scheme given in table 8 is based on the solution of cobalt metal. This scheme is less complex than the one using CoO(c) ; however, the two methods agree within the limits of experimental error. A slight pressure increase in the reaction vessel was noted on disassembly following the solution of cobalt metal. Since cobalt may be oxidized by hydrogen ions as well as

tribromide ions, the pressure increase noted was probably caused by residual hydrogen gas. From thermodynamic considerations, hydrogen gas would be readily oxidized by the tribromide present; however, the kinetics of this reaction are relatively slow without a suitable catalyst. The accuracy of scheme 1, based on the oxide (table 7), is preferred because of the uncertainty in assuming that possible hydrogen formed is completely oxidized in reaction 2 of table 8.

TABLE 7. - Calorimetric reaction scheme for $\text{CoS}_{0.89}\text{(c)}$ at 298 K

Reaction ¹	ΔH° , kcal	Uncertainty, kcal
(1) $\text{Co}^{++} + 7.112\text{H}^+ + 11\text{Br}^- + 0.89\text{SO}_4^{2-} = \text{CoS}_{0.89}\text{(c)} + 3.667\text{Br}_3^- + 3.556\text{H}_2\text{O}$	96.52	1.32
(2) $\text{CoO(c)} + 2\text{H}^+ = \text{Co}^{++} + \text{H}_2\text{O}$	-26.37	.29
(3) $0.89\text{S(c)} + 2.667\text{Br}_3^- + 3.556\text{H}_2\text{O} = 0.89\text{SO}_4^{2-} + 7.112\text{H}^+ + 8\text{Br}^-$	-78.45	1.5
(4) $2(\text{HBr} + 20.75\text{H}_2\text{O})(\text{l}) = 2\text{H}^+ + 2\text{Br}^- + 41.5\text{H}_2\text{O}$	0	.01
(5) $\text{H}_2\text{O(l)} = \text{H}_2\text{(g)} + 0.5 \text{O}_2\text{(g)}$	68.315	.010
(6) $42.5\text{H}_2\text{O} = 42.5\text{H}_2\text{O(l)}$	.932	.02
(7) $\text{H}_2\text{(g)} + \text{Br}_2\text{(l)} + 41.5\text{H}_2\text{O(l)} + 2(\text{HBr} + 20.75\text{H}_2\text{O})(\text{l})$	-56.92	.05
(8) $\text{Co(c)} + 0.5 \text{O}_2\text{(g)} = \text{CoO(c)}$	-56.76	.10
(9) $\text{Br}_3^- = \text{Br}_2\text{(l)} + \text{Br}^-$	2.1	.50
(10) $\text{Co(c)} + 0.89\text{S(c)} = \text{CoS}_{0.89}\text{(c)}$	-50.63	2.1

¹Reaction enthalpies are corrected to 298.15 ± 0.5 K. All reaction species are in solution unless otherwise noted.

TABLE 8. - Calorimetric reaction scheme for $\text{CoS}_{0.89}\text{(c)}$ using Co(c) at 298 K

Reaction ¹	ΔH° , kcal	Uncertainty, kcal
(1) $\text{Co}^{++} + 7.112\text{H}^+ + 11\text{Br}^- + 0.89\text{SO}_4^{2-} = \text{CoS}_{0.89}\text{(c)} + 3.667\text{Br}_3^- + 3.556\text{H}_2\text{O}$	96.52	1.32
(2) $\text{Co(c)} + \text{Br}_3^- = \text{Co}^{++} + 3\text{Br}^-$	-69.71	.85
(3) $0.89\text{S(c)} + 2.667\text{Br}_3^- + 3.556\text{H}_2\text{O} = 7.112\text{H}^+ + 0.89\text{SO}_4^{2-} + 8\text{Br}^-$..	-78.45	1.5
(4) $\text{Co(c)} + 0.89\text{S(c)} = \text{CoS}_{0.89}\text{(c)}$	-51.64	2.2

¹Reaction enthalpies are for 298.15 ± 0.5 K. All reaction species are in solution unless otherwise noted.

DISCUSSION

No previous low-temperature heat capacities of $\text{CoS}_{0.89}$ have been reported in the literature.

Schchelkotunov (6) has reported measuring the heat capacities of $\text{CoS}_{1.33}$ in the temperature range 173 to 673 K using an adiabatic calorimeter. By interpolation from his graphs, the heat capacity of $\text{CoS}_{1.33}$ was estimated at $12.5 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ at 300 K.

Ogawa (7) measured the heat capacity of CoS_2 in the nominal range of 20 to 320 K by adiabatic calorimetry and found a sharp lambda-type anomaly in the C_p curve with a maximum of 121.2 K. The magnetic contribution to the entropy resulting from this transition was reported as $0.40R\ln 2$ per mole CoS_2 . Because of the scaling of Ogawa's graphs, no pretransition maximum in the data is evident, as was observed around 114 K in the present investigation.

Waki (8) in a short note reported the heat capacity of CoS_2 from about 4.9 to 8 K. The data in this report were also presented graphically and agree fairly well over this limited range with the results of this investigation.

Mills (16) estimated the standard entropies at 298.15 K of $\text{CoS}_{0.89}$, $\text{CoS}_{1.33}$, and CoS_2 as 12.5 ± 1 , 14.7 ± 2 , and $16.5 \pm 1.5 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively, from high-temperature vapor pressure measurements of various investigators. The standard entropy values for these sulfides, derived from heat capacity data in the present investigation, are 10.36 ± 0.02 , 12.96 ± 0.03 , and $16.31 \pm 0.03 \text{ cal}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, respectively.

The ΔH_f° of $\text{CoS}_{0.89}$ was determined as $-50.63 \pm 2.1 \text{ kcal}\cdot\text{mol}^{-1}$ by reaction solution calorimetry. Most of the formation enthalpy values for $\text{CoS}_{0.89}$ reported in the literature were derived from indirect vapor-pressure measurements at high temperatures. Mills (16) selected $-22.6 \pm 1 \text{ kcal}\cdot\text{mol}^{-1}$ for ΔH_f° of $\text{CoS}_{0.89}$ at 298 K, based on gas equilibrium measurements of Rosenqvist (2), Alcock (3), and Kolbina (4). More recent vapor pressure measurements by Lau and Hildenbrand (17) on a mixture of approximately 20 wt pct Co and 80 wt pct $\text{CoS}_{0.89}$ resulted in an estimate of $-35.2 \text{ kcal}\cdot\text{mol}^{-1}$ for ΔH_f° of $\text{CoS}_{0.89}$. The cause of the large discrepancy between results of the present investigation and the formation enthalpies derived by second-law treatments of gas equilibria data is not readily apparent. The difference is too large to attribute to errors in vapor pressure determinations or intrinsic extrapolation errors. The high-temperature solid phase in equilibrium with the gaseous species in these studies would have to deviate substantially from the assumed $\text{CoS}_{0.89}$ surface composition.

Examination of the present investigation for possible sources of error reveals an unexpectedly low (less negative) value for the solution enthalpy of $\text{CoS}_{0.89}$ in reaction 1 as compared with -105 kcal for CuS in previous measurements by Stuve (11). Since the method of acidic bromine solution calorimetry for sulfides is relatively new, it is difficult to assign with certainty the probable cause for the dissimilitude of formation enthalpies.

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